SCIENCE FOR GLASS PRODUCTION

UDC 666.1.031:666.1.022

NEW CONCEPTS OF GLASS-MELTING PROCESSES

V. F. Solinov[1]

Translated from Steklo i Keramika, No. 10, pp. 5 – 7, October, 2004.

A method for melting glass in a direct monohomogeneous thin flow of mechanochemically activated batch is proposed, which makes it possible to obtain homogeneous defect-free glass melt and intensify all stages of the glass-melting process.

The problem of glass strength that has been traditionally addressed in producing vehicle and especially aircraft glazing is currently becoming acute for civil engineering glazing. None of the domestic glass industry standards have even prescribed the strength of glass. As a consequence of its low strength, not more than 60% of the total building glass produced is put into service, while the rest is lost in the course of storage, transportation, and installation. The present increase in the size of architectural glass parts known as "jumbo" causes new problems, such as increasing probability of encountering defects in a large glass sheet, more complicated transport and assembly operations, and the need to increase the service reliability of products. The application areas for sheet glass requiring increased reliability keep expanding: staircase, elevator, and road enclosures, large-area ceilings, floors, stairs, even some attempts to make a transparent car cabin.

It is known that the theoretical strength of defect-free glass is 25,000 – 35,000 MPa. It can be assumed that the actual strength of sheet glass at the initial stage of the float-formation process can be of the order of 6000 – 8000 MPa, which is similar to the strength of glass fibers whose surface immediately after drawing from a platinum spinneret is coated by a special protective layer. As the glass ribbon moves along the float-tank and then through the annealing furnace, such factors as dust, chemical reaction of the bottom surface with the tin (oxide) melt, scratches inflicted by rollers, etc., not to mention the defects caused in industrial treatment of glass, bring its strength down to 30 – 60 MPa. Therefore, one of the methods for producing high-strength glass is preserving its high strength not only at all process stages, but in service as well. This implies the protection of glass surface by coatings preventing its mechanical or chemical damage. For instance, in annealing of glass with temporary technological or other coatings deposited it is possible to obtain plates with residual strength of 700 – 1000 MPa. Such protection may be even more significant if it persists in the course of service. Note that construction parts without such protection gradually lose their strength due to abrasive effects and under the impact of atmospheric precipitation.

In general the strength of glass depends on two main groups of defects:

– defects of the surface and near-surface layers of the glass ribbon;

– glass melt defects.

The defects of glass surface and near-surface layers are the best studied. It is established that they have a deciding effect on the strength level. It is established that they have a deciding effect on the level of strength. A modification of the glass composition affects the strength to a lesser extent.

The surface defects can be classified according to the depth of their location. For glass of thickness 5 – 6 mm they can be located at a depth up to 10 – 15, at 30 μm, or up to 0.5 mm. The first of the specified defects are mainly Griffith microcracks, the second are defects inflicted in production, transportation and service, and the third are inclusions, bubbles, etc. Some deep effects are the consequences of needle-shape crystals sticking to the glass ribbon on the first and second roller after the float-tank.

The choice of the glass hardening method and its final strength depend on the depth at which the defects are located. The depth of the defects is less significant for glass hardening than for ion-exchange strengthening and pickling. The maximum strengthening effect is reached when the glass defects are removed from the maximum depth.

[1] Research and Development Institute of Technical Glass (NIITS), Moscow, Russia.

0361-7610/04/0910-0320

Successful improvement in the strength of glass has been demonstrated in long-term practice of the Research and Development Institute of Technical Glass and other institutes. The industrial strengthening methods include traditional air hardening; ion exchange that has proved its technological possibilities; pickling used in making impact-resistant aircraft glazing withstanding collision with birds and bullet and splinter impacts, and all possible combinations of the above methods.

Achieved Levels of Glass Strength

Glass	Bending strength, MPa
Initial	30 – 80
Strengthened glass:	
air hardening	120 – 180
liquid hardening	200 – 400
ion exchange	300 – 500
pickling	1000 – 1700
combined methods	1500 – 2000

However, considering that the reserves of glass strengthening by surface modifications or by creating compressive stresses are virtually exhausted, the problem of producing a homogeneous defect-free glass melt becomes the critical one.

Unfortunately, the effect of glass structure and its macro- and microstructural inhomogeneities on strength are less well studied, since any operation in sheet glass production (composition and method of batch preparation, quantity of recyclable cullet, quality of furnace refractories, furnace design, melting temperature, etc.) may affect the quality of glass melt.

In joint research of the NIITS and the Saratov Institute of Glass it was established (Fig. 1) that as the content of recycled cullet in a batch grows to 50%, the strength of melted glass sharply decreases, its brittleness increases (which is known as “dry glass”), and hardness decreases. With a further increase in the cullet content up to 100% the hardness is restored only partially. Presumably the content of cullet in the batch equal to 50 – 60% is the worst for getting homogenous glass. An example of such inhomogeneity are crystal-like structures in glass, which are revealed in pickling the surface to a depth of 0.5 mm.

Traditionally, the domestic and world glass-melting industry uses the same glass-melting method based on melting batch and cullet loaded into the furnace and subsequent stages of silicate formation, glass formation, clarification, and homogenization. The traditional glass-melting method requires high energy consumption due to nonproductive heat consumption to maintain the required temperature of a large melt volume constantly present in the furnace tank and large capital investments in the furnace construction due to a large capacity of their melting tanks.

Moreover, disadvantages of this technology include the long duration of the glass-melting, homogenization and clarification processes, the presence of powerful uncontrollable convection flows transferring substantial quantities of heat from the melting part of the tank to the cooling part, the need to maintain high melting temperatures which in some cases surpass the possibilities of the contemporary refractories.

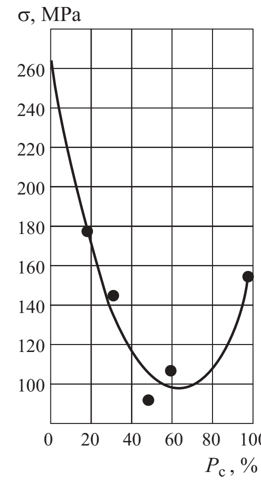

Fig. 1. Dependece of mechanical strength of glass σ on cullet content P_c in the batch.

Considering the above disadvantages, it is possible to state the main requirements on improving the glass-melting technology:

– decreasing specific power consumption by transferring the reactions between the batch components out from the furnace and the viscous glass-melt medium; decreasing the volume of the inert part of the melt that consumes up to 80 – 90% of supplied heat to maintain its temperature;

– developing optimum conditions for all glass-formation stages in each microvolume of the active part of the melt and the possibility of their regulation.

The above requirements are best of all satisfied by producing glass by melting a batch on a sloping tray, glass formation in a thin overheated layer, and its homogenization by forced stirring proposed in USSR Inventor’s Certificate No. 48551. However, the idea of accelerating the homogenization of the melt by its stirring in a thin layer is hard to implement, moreover, overheating of this melt will inevitably facilitate the formation of secondary gaseous bubbles, which delays the clarification process.

A team of authors (V. F. Solinov, et al.) proposed a glass melting method (Eurasian patent No. 004516, dated April 29, 2004) which can provide a homogeneous defect-free glass melt in a direct monohomogeneous thin flow. A traditional initial batch arrives from a bunker into a mechanical dispenser, is compressed as a plate and fed into the glass-melting unit and then into the float-tank.

The batch preparation processes require a special consideration. The traditional technology includes such operations of separate preparation of materials as drying, concentration, and milling, after which the batch components are mixed with glass cullet in a prescribed ratio. The batch is briquetted or granulated and arrives into the furnace.

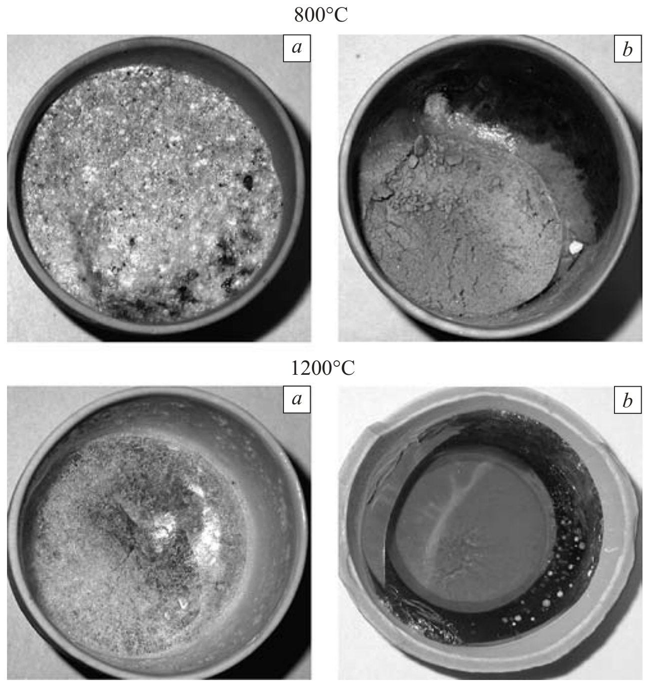

Fig. 2. The results of melting traditionally prepared (*a*) and mechanochemically activated (*b*) batch at different temperatures.

There also exist the hydrothermal synthesis method for vitreous and crystalline materials and the sol-gel technology based on preliminary production of suspensions or colloid solutions of material components, but their application is restricted as they involve complicated, expensive and, which is especially significant, low-efficiency equipment. It should be noted that using these methods for material preparation decreases the temperature of subsequent processes needed to produce the final material, and this advantage is widely used in depositing tinted coatings on sheet glass.

The mechanochemical activation of solid materials is rather well known. Finely dispersed powder intensely milled by impact actions enters more actively into solid-phase reactions with other milled materials due to its highly extended contact surface with nonsaturated chemical bonds and active radicals.

We took this method as a basis and introduced significant modifications. The point of the method is that the batch of traditionally prepared and mixed components, including cullet, is subjected to further superfine milling with the addition of special temporary reactants. Such preparation of the batch ensures its homogeneity, the initial stages of silicate-formation reactions occurring in mixing, i.e., outside the furnace, and their fast completion in the beginning of the melting zone. We have calculated the thermal power supplied per 1 m^2 of the batch-melting and reaction-clarification zones depending on batch loading and the ratio between the charging front width and the length of the reaction-clarification zone. Experiments corroborating these calculations have been performed.

The calculation, model and bench tests of the melting set, and prototype meltings using specially prepared batches demonstrated the advantages of the new technology:

– absence of glass-melt homogenization zone;

– a decrease in thermal inertia and power consumption of the process due to decreasing the total weight of the melt and an increase specific weight of its active part participating in glass melting;

– a decrease by 150 – 200°C in the temperature of the high-temperature process stages (Fig. 2);

– acceleration of all process stages due to a unified working flow and eliminating the spontaneous reverse glass melt currents;

– intensification of glass melting due to two-sided heat supply to the melt (gas heating from above and electric heating from beneath);

– the possibility of local thermal adjustment of at each stage of the process;

– the possibility of controlling the composition of the redox atmosphere in the melting space;

– the possibility of a simplified readjustment of the melting set when the thickness and width of the glass ribbon or the chemical composition of glass change.

The proposed processes can be primarily used for limited-volume production of specialized and plated glass, including photochrome and heat-absorbing glass. A further development of this technique can have a significant effect on the mass-scale industrial production of glass.

The possibility of producing glass based on the technology proposed changes and expands the existing concepts of the glass-melting stages and their sequence. In particular, it follows from the above description that the silicate-formation stage is divided into two phases. The preliminary phase is implemented outside the glass-melting furnace in the course of fine milling mechanochemical activation of components, mixing, and moistening of batch, which creates conditions for solid-phase silicate-formation reactions. The final stage of silicate formation proceeds in the melt. The same is true of the homogenization stage, since thorough mixing of batch components at the first (outside the furnace) stage already ensures increased homogeneity of the future melt, which is finally achieved in the furnace.

Our institute continues research contributing to the modification of the remaining glass-melting stages and developing efficient equipment for this purpose, which will makes it possible to change from the classic glass-melting method to a new technology of producing glass, and not only sheet glass.